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ESR Study of Radical Halogen Abstractions. Participation of Electron-Transfer Mechanism in the Radical Halogen Abstractions

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The halogen-abstraction reactions of carbon radicals were investigated as a model of the chain-transfer reaction in the radical polymerization of vinyl compounds. The kinetics of the halogen-abstraction reaction of carbon radicals ($(CH_3)_2\dot{C}X$, X=OC_6H_5, $OCOCH_3$, SC_6H_5, C_6H_5, and CN) from tetrahalomethanes(CBr_4, $CBrCl_3$, CCl_4) were studied in toluene at 80 °C by the ESR method using 2-(*t*-butyl)thioacrylonitrile as a spin-trapping reagent. The reactivity of these radicals for each halomethane decreased in the order X: $OC_6H_5 > OCOCH_3 > SC_6H_5 > C_6H_5 > CN$ The reactivity of tetrahalomethanes for each radical decreased in the order $CBr_4 > CBrCl_3 > CCl_4$. Results are explained by taking into account the electron-transfer process from carbon radicals to tetrahalomethanes. Absolute rate constants of the halogen abstraction of $(CH_3)_2\dot{C}CN$ and $(CH_3)_2\dot{C}C_6H_5$ from CBr_4 and $CBrCl_3$, and of their additions to 2-(*t*-butylthio)acrylonitrile were estimated by the spin-trapping method, and they were compared with available data for similar reactions.

It has been reported that the solvent effect on the propagation rate constant k_p of vinyl esters, which have negative e values, is opposite in trend to that of methacrylates, which have positive e values. A proposal was made that the solvent effect could be explained in terms of donor-acceptor complexes of the propagating radicals with aromatic solvents[1—5] In these cases, the propagating radicals of methacrylates($e > 0$) were considered to be electron acceptors to the aromatic solvents and those of vinyl esters($e < 0$) to be electron donors to the solvents. This opposite trend in the reactivity of the propagating radicals between methyl methacrylate(MMA) and vinyl acetate(VAc) was also found in chain-transfer reactions to CCl_4 and triethylamine:[6—9] CCl_4 showed higher reactivity to the propagating radical of VAc and triethylamine to that of MMA. These facts suggest that the reactions proceed through a donor-acceptor complex formation or an electron-transfer process.

Recently, the participation of the electron-transfer process in radical reactions was pointed out in ESR studies on the reaction of the hydroxymethyl radical with CCl_4,[10,11] and in a flash photolysis on the reaction of the triethylsilyl radical with tetrahalomethanes.[12] Other examples supporting the electron-transfer process might be the chain-transfer reaction to strong transfer reagents in the radical polymerization. Since the occurrance of a net electron transfer indicates that a free radical can be converted to an ion, the finding of such a reaction seems to afford a new possibility for the reaction control of the radical polymerization. In order to investigate the possibility of the electron transfer of free radicals, we studied the reaction of free radicals with electron-accepting chain-transfer reagents, such as CBr_4 and $CBrCl_3$.

In this paper, we will repoprt an ESR study on the chain-transfer reactions of model radicals of the propagating end to tetrahalomethanes and discuss the participation of the electron-transfer process in the radical reactions. The radicals obtained by the chain-transfer reaction were trapped by 2-(*t*-butylthio)acrylonitrile which was found by Viehe as a strong radical scavenger.[13] Moreover, a new method for a determination of the rate constant of the chain transfer will be proposed.

Experimental

ESR spectra were recorded on a Japan Electron Optics Laboratory Model JES-FE 1X ESR spectrometer with a variable temperature accesory (ES-VT-3A) under irradiation with a 500 w high-pressure mercury lamp (Ushio 500) at 80 °C. A solution of azo compound 5×10^{-2} M, trapping reagent 6.4×10^{-1}—3.9×10^{-3} M, and tetrahalomethane 1.1×10^{-1}—9.8×10^{-4} M in toluene (1 ml) in a quartz sample tube (3 mmϕ) was degassed by repeated melting and freezing under vacuum and then sealed.

UV spectra were measured on a Hitachi 124 UV-visible spectrometer.

2,2′-Azobisisobutyronitrile(AIBN) was recrystallized from ethanol. 2,2′-Diacetoxy-2,2′-azopropane, 2,2′-bis(phenylthio)-2,2′-azopropane, and 2,2′-diphenoxy-2,2′-azopropane were prepared by the method of Benzing et al.[14] Azocumene was prepared from α-cumenamine and IF_5 by the method of Bartlet et al.[15] 2-(*t*-Butylthio)acrylonitrile was prepared according to the method of Viehe et al.[16]

CBr_4 was recrystallized from hexane. $CBrCl_3$(104 °C/760 mmHg(1 mmHg=133.322 Pa)) and CCl_4 (76.6 °C/760 mmHg) were purified by distillation. Hexamethylbenzene for the measurement of the electron affinity was sublimed twice. Toluene was dried and distilled by the conventional method. 2,2,6,6-Tetramethyl-1-piperidinyloxyl (Tempol)[17] was purified by recrystallization from cyclohexane.

An estimation of the kinetic parameter was carried out by a computer calculation using a nonlinear least-squares method, computer program of which was Sals II written by Nakagawa and Koyanagi(Tokyo University Program). The simulation for the overlap of two adducts was carried out by a JEOL ESR simulation program 0398.

Results

Addition Reaction of Carbon Radicals to 2-(*t*-Butyl)thioacrylonitrile. Figure 1 shows the ESR spectrum observed under irradiation of a mixture of AIBN and 2-(*t*-butylthio)acrylonitrile, a spin-trapping reagent(T). The ESR spectrum of a triplet of triplets with hyperfine splitting constants of 0.88 and 0.28 mT due to nitrogen and two equivalent protons, respectively, was assigned to the adduct of $(CH_3)_2\dot{C}CN$ to T. Similar spectra were observed in the systems of other azo compounds and T. The hyperfine splitting constants of the adducts are shown in Table 1. The change in the ESR spectrum with reaction time shows that the concentration of the adduct became stationary within several minutes after irradiation. The signal due to the radicals (M·) of azo compounds (Eq. 1) could not be detected, indicating that the stationary concentration of M· was negligibly small compared with the adduct(MT·). Therefore, the bimolecular self-termination of M· was not taken into account in the kinetic treatment. Thus, the reactions are shown in Eqs. 1 to 4.

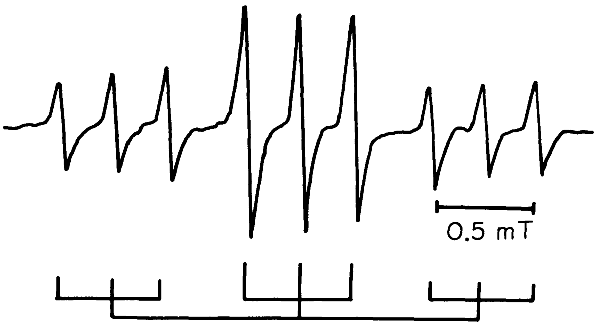

Fig. 1. ESR Spectrum observed on irradiation of a mixture of AIBN and 2-(*t*-butylthio)acrylonitrile(T) in toluene at 80 °C.
[AIBN]=5×10^{-2}M, and [T]=0.64 M.

Table 1. Hyperfine Splitting Constants for Adducts Obtained by Reaction of Carbon Radicals with 2-(*t*-Butylthio)acrylonitrile[a]

Radicals		a_H/mT	a_N/mT
$(CH_3)_2\dot{C}X$	X=-CN	0.88	0.28
	$-C_6H_5$	0.93	0.28
	$-OCOC_6H_5$	0.94	0.28
	$-SC_6H_5$	0.92	0.28
	$-OC_6H_5$	0.95	0.27
$\dot{C}Cl_3$		0.80	0.26
$\dot{C}Br_3$		0.77	0.26

a) 80 °C in toluene.

$$\text{M-N=N-M} \xrightarrow{I} \text{M}\cdot, \qquad I\text{: Rate} \tag{1}$$

$$\text{M}\cdot + \text{T} \xrightarrow{k_1} \text{MT}\cdot, \tag{2}$$

$$\text{MT}\cdot + \text{M}\cdot \xrightarrow{k_2} \text{Product}, \tag{3}$$

$$\text{MT}\cdot + \text{MT}\cdot \xrightarrow{k_3} \text{Product}. \tag{4}$$

The assumption of the steady state for the concentrations of M· and MT· leads to Eq. 5:

$$[\text{T}] = \frac{(k_2/k_1)[\text{MT}\cdot](1+k_3/I[\text{MT}\cdot]^2)}{1-k_3/I[\text{MT}\cdot]^2} \tag{5}$$

The relation between the stationary concentrations of MT· and T is shown in Fig. 2. The ratios, k_2/k_1 and k_3/I, were determined from Eq. 5 by a computation using the data shown in Fig. 2. The obtained ratios are shown in Table 2. The k_1/k_2 were influenced by substituents at the α-position, decreasing in the order:

$-OC_6H_5 > -OCOCH_3 > -SC_6H_5 > -C_6H_5 > -CN$.

The values of k_3/I changed remakably with the substituents.

Halogen Abstraction Reaction of Carbon Radicals from Tetrahalomethane. The intensity of the ESR spectra of the mixture of $CBrCl_3$, AIBN, and T was not large enough to perform a kinetic study in the absence of UV irradiation at 80 °C. Figure 3 shows the ESR spectrum observed upon irradiating the mixture. The spectrum (Fig. 3) was an overlap of two kinds of triplets of triplets, which were assigned

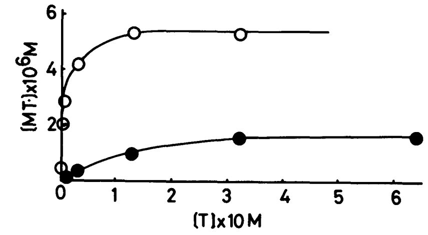

Fig. 2. Relation between MT· and T Concentrations.
○: 2,2'-Diacetoxy-2,2'-azobispropane, ●: AIBN.
[AIBN]=5×10^{-2} M.

Table 2. Kinetic Data in Addition Reaction of Free Radicals $(CH_3)_2\dot{C}X$ to 2-(*t*-Butylthio)acrylonitrile[a,b]

X	$k_1/k_2/10^{-4}$	$k_3/I/10^{10}$ M^{-2}
-CN	0.10	39
$-C_6H_5$	0.38	43
$-OCOCH_3$	3.6	450
$-SC_6H_5$	3.1	2.6
$-OC_6H_5$	4.4	2.2

a) 80 °C in toluene, [M-N=N-M]=5×10^{-2} M. b) Average values of 3—5 runs(mean deviation ±50%).

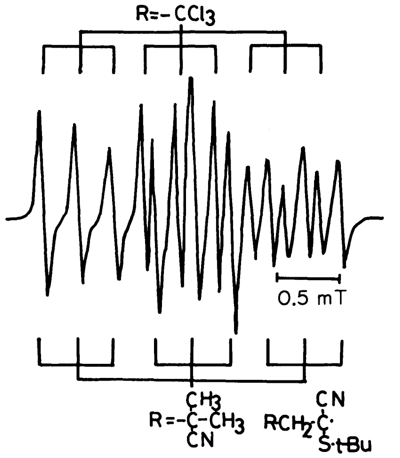

Fig. 3. ESR Spectrum observed on the UV irradiation of a mixture of $CBrCl_3$, AIBN, and 2-(*t*-buthylthio) acrylonitrile in toluene at 80 °C. $[CBrCl_3]=8.8\times10^{-2}$ M, $[AIBN]=10^{-2}$ M, and $[T]=0.32$ M.

to the adducts of the 1-cyano-1-methylethyl radical and of the trichloromethyl radical produced from AIBN and by bromine abstraction from $CBrCl_3$, respectively. Similar spectra were observed in other systems of tetrahalomethanes, azo compounds, and T. The hyperfine-splitting constants of the adducts are shown in Table 1. The reactions are illustrated in the following equations.

$$\text{M-N=N-M} \xrightarrow{I} \text{M}\cdot, \tag{1}$$

$$\text{M}\cdot + \text{T} \xrightarrow{k_1} \text{MT}\cdot, \tag{2}$$

$$\text{M}\cdot + \text{RX} \xrightarrow{k_x} \text{MX} + \text{R}\cdot, \tag{6}$$

$$\text{R}\cdot + \text{T} \xrightarrow{k_{1x}} \text{RT}\cdot, \tag{7}$$

$$\text{RT}\cdot + \text{RT}\cdot \xrightarrow{k_3} \text{RTTR}, \tag{8}$$

$$\text{RT}\cdot + \text{MT}\cdot \xrightarrow{k_3} \text{MTTR}, \tag{9}$$

$$\text{MT}\cdot + \text{MT}\cdot \xrightarrow{k_3} \text{MTTM}. \tag{10}$$

Since M· and R· were not observed in the ESR spectra, the self-coupling reactions of these radicals were not taken into account. A stationary state treatment on R·, RT·, and MT· gives

$$\frac{[\text{RT}\cdot]}{[\text{MT}\cdot]} = \frac{k_{1x}}{k_1}\frac{[\text{R}\cdot][\text{T}]}{[\text{M}\cdot][\text{T}]} = \frac{k_x}{k_1}\frac{[\text{RX}]}{[\text{T}]}. \tag{11}$$

Two examples of a plot of [RT·]/[MT·] vs. [RX] are shown in Fig. 4. Linear relations were observed, the ratios, k_X/k_1, being calculated from the slopes. Results are shown in Table 3. Since the signal MT· was not observed in the reactions of the radicals X=-CN, $-C_6H_5$, and $-OCOCH_3$ with CCl_4, the ratios could not be estimated. This fact indicates that k_x is too small for the ESR spectrum to be detected. From a comparison of k_x/k_1 for the reactions of a given radical with CBr_4, $CBrCl_3$, and CCl_4, it is concluded that rate constants for the halogen abstraction decrease in the order, $CBr_4 > CCl_3Br > CCl_4$, in all reaction systems.

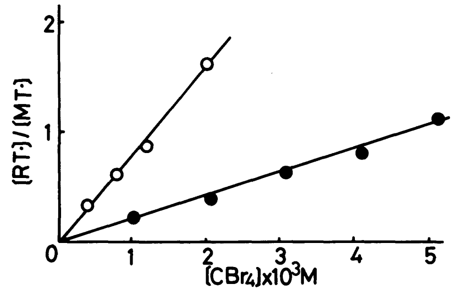

Fig. 4. Plot of [RT·]/[MT·] versus $[CBr_4]$ in the stationary concentrations of RT· and MT·.
○: 2,2'-Phenoxy-2,2'-azopropane, ●: 2,2'-phenylthio-2,2'-azopropane.
$[\text{M-N=N-M}]=5\times10^{-2}$ M, and $[T]=0.32$ M.

Table 3. Relative Rate Constants for Radicals $(CH_3)_2\dot{C}X$ in Halogen Abstraction[a,b)]

X	k_x/k_1		
	CBr_4	$CBrCl_3$	CCl_4
-CN	4.9	0.21	—
$-C_6H_5$	2.4	0.61	—
$-OCOCH_3$	200	15	—
$-SC_6H_5$	56	5.3	0.0075
$-OC_6H_5$	210	89	2.2

a) 80 °C in toluene, $[\text{M-N=N-M}]=5\times10^{-2}$ M. b) Average value of 3—5 runs(mean deviation ±10%).

A remarkable difference in k_x/k_1 was found in the reactions of different radicals with a given tetrahalomethane. However, since k_1 are not considered to be constant, no information regarding k_x could be obtained from k_x/k_1.

Absolute Rate Constants for Elementary Steps. Since the kinetic parameters obtained so far were k_x/k_1, k_2/k_1, k_x/k_2 and k_3/I, absolute rate constants of each elementary processes could not be directly estimated. If the k_2 could be evaluated, k_1 and k_x could be estimated. It is difficult to directly measure k_2. However, if the self-coupling constants of M· and MT· are determined, rate constants of the cross-coupling reactions can generally be estimated as the geometrical mean of the self-coupling rate constants:[18)]

$$k_2 = (k_3k_M)^{1/2} \tag{12}$$

where k_M and k_3 are the rate constants for the self-coupling reactions.

In order to estimate k_3 from k_3/I, I for each azo compound was estimated by the following method. Carbon radicals are known to be quantitatively trapped by *N*-oxyl radical such as 2,2,6,6-tetramethyl-1-piperidinyloxyl(Tempol).[19] Accordingly, I for all azo compounds were determined from measurements of the decreasing rates of Tempol which were added to the reaction system. The rates were estimated from the change in the signal intensity of the ESR spectrum with time. The values of k_3 were calculated from k_3/I and I was thus obtained. I and k_3 are shown in Table 4. The k_3 values obtained are of the same order for all systems; this indicates that this method leads to reasonable data because k_3, which is the reaction rate constant of a diffusion-controlled reaction, should be constant, at least regarding the order of magnitude in all systems. I changed remarkably with the substituent. This change might be due to a difference in the light intensity, the molecular extinction coefficients of the azo compounds, the extent of the contribution of thermal decomposition, or the efficiency of Eq. 2.

The values of k_M for $(CH_3)_2\dot{C}C_6H_5$ and $(CH_3)_2\dot{C}CN$ have been reported in the literature.[20,21] The k_2 values for these radicals were estimated from Eq. 12 using k_3 and k_M (Table 6). Since k_M for the other radicals has not yet been reported, k_1 and k_x for only two radicals were estimated by a substitution of k_2 for k_1/k_2 and k_x/k_2 and are shown in Tables 5 and 6.

Table 4. Rate Constants of the Coupling Reaction of the Adduct and Rates of Formation of Radicals ($(CH_3)_2\dot{C}X$)[a,b]

X	$k_3/10^8$ $M^{-1}\,s^{-1}$	I[b)] $M\,s^{-1}$
$-CN$	3.5	9.0×10^{-4}
$-C_6H_5$	7.0	1.6×10^{-3}
$-OCOCH_3$	6.6	1.5×10^{-4}
$-SC_6H_5$	8.7	3.5×10^{-2}
$-OC_6H_5$	7.0	1.6×10^{-3}

a) 80 °C in toluene, $[M\text{-}N{=}N\text{-}M]=5.0\times10^{-2}$ M. b)
b) Average values of 3—5 runs(mean deviation ±30%).

Table 5. Rate Constants of the Addition Reaction and Coupling Reactions[a)]

$(CH_3)_2\dot{C}X$	$k_1/10^4\ M^{-1}\,s^{-1}$	$k_2/10^8\ M^{-1}\,s^{-1}$
X=CN	0.84	8.4
C_6H_5	1.2	24

a) 80 °C in toluene.

Table 6. Rate Constants of the Halogen Abstraction of $(CH_3)_2\dot{C}X$ from tetrahalomethanes[a)]

X	$k_x/10^5\ M^{-1}\,s^{-1}$		
	CBr_4	$CBrCl_3$	CCl_4
$-CN$	4.1	0.17	—
$-C_6H_5$	22	5.5	—

a) 80 °C in toluene.

Discussion

Reactivity of Model Radicals in Addition Reaction to 2-(*t*-Butylthio)acrylonitrile and Halogen Abstraction. Since the absolute rate constants for an addition reaction(k_1) and a halogen abstraction(k_x) were determined for only two kinds of radicals, it is difficult to discuss the mechanism of the addition reaction and a chain-transfer reaction by a comparison of k_1 and k_x. However, since the bimolecular reactions between M· and MT· are diffusion-controlled in all reaction systems, k_2 are reasonably assumed to be constant, at least regarding the order of magnitude, in all reaction systems. Therefore, k_1/k_2 is considered to represent the reactivity of M· in Eq. 2. The reactivities of the radicals were influenced by substituents at the α-position; these decreased in the order:

$$-OC_6H_5 > -OCOCH_3 > -SC_6H_5 > -C_6H_5 > -CN.$$

This order shows that the radicals binding to heteroatoms have a larger reactivity than those stabilized by a phenyl or cyano group. The difference in the reactivity between $-OC_6H_5$ and $-OCOCH_3$, or between the phenyl and cyano groups, seems to be explained by the polarity of the substituent: the radicals binding to more electrodonating substituent have a higher reactivity.

Any information concerning the reactivity of model radicals in a halogen-abstraction reaction could not be obtained from k_x/k_1. However, it is possible to discuss the reactivity of a given radical with k_x/k_2 (Table 7), because k_2 is considered not to be influenced by the halomethanes used. Therefore, k_x/k_2 ratios were estimated from the k_x/k_1 and k_1/k_2 obtained in the last section. The values of k_x/k_2 are shown in Table 7, and decrease in the following order:

$$-OC_6H_5 > -OCOCH_3 > -SC_6H_5 > -C_6H_5 > -CN.$$

Table 7. Relative Rate Constants of Radicals $(CH_3)_2\dot{C}X$ in Halogen Abstractions[a)]

X	k_x/k_2		
	CBr_4	$CBrCl_3$	CCl_4
$-CN$	0.49	0.02	—
$-C_6H_5$	0.91	0.23	—
$-OCOCH_3$	720	54	—
$-SC_6H_5$	170	16	0.0075
$-OC_6H_5$	920	390	9.7

a) 80 °C in toluene, $[M\text{-}N{=}N\text{-}M]=5\times10^{-2}$ M.

This order shows that the carbon radicals binding to heteroatoms have a larger reactivity for halogen abstraction than radicals stabilized by phenyl or cyano groups. From Table 7, it is concluded that the rate constants for reaction between a given radical and tetrahalomethanes increase in the order $CCl_4 < CBrCl_3 < CBr_4$. For example, the reaction rate of $(CH_3)_2\dot{C}OC_6H_5$ and $(CH_3)_2\dot{C}SC_6H_5$ with CBr_4 was 10^2—10^3 times as large as that with CCl_4.

It has been reported that the activation energy of the halogen abstraction of free radicals from halomethane can be estimated from their bond dissociation energies(BDE) by the following relation[22]:

$$E = 0.055 \times [\mathrm{BDE}] \tag{13}$$

If the preexponential factors are assumed to be the same in halogen-abstraction reactions of a given radical from tetrahalomethanes, k_x/k_1 for CBr_4 is calculated to be less than 10-times as large as that for CCl_4(C–Cl 67.9 kcal mol^{-1}(1 cal=4.184 J), and C–Br 45—57 kcal mol^{-1}),23) the difference being much smaller than that observed. If the reaction mechanism is the same in all halogen-abstraction reactions, the preexponential factor is considered to be in the same order of magnitude24) because tetrahalomethanes are composed of the same number of atoms. This large difference in k_x among halomethanes may be due to a difference in the reaction mechanism. Accordingly, we investigated the possibility of an electron-transfer mechanism in halogen-abstraction reactions of carbon radicals from tetrahalomethanes.

Electron-Transfer Mechanism. First, the electron affinities(EA) were estimated from the absorption spectra of their complexes with hexamethylbenzene by the method of Hatano et al.25) Results are shown in Table 8, indicating that EA decreases in the order

$$CBr_4 > CCl_3Br > CCl_4.$$

This order is in agreement with the order of rates for halogen abstraction.

The reactivity of each radical with a given tetrahalomethanes was estimated by k_x/k_2 (Table 7), decreasing with the α-substituents in the following order:

$$\text{-}OC_6H_5 > \text{-}OCOCH_3 > \text{-}SC_6H_5 \gg \text{-}C_6H_5 > \text{-}CN.$$

The ratio for CBr_4 and $(CH_3)_2\dot{C}OC_6H_5$ which has an electron-donating group is about 2000 times as large as that for CBr_4 and $(CH_3)_2\dot{C}CN$, which has an electron-accepting group. Therefore, the electron-donating power of free radicals is considered to be an important factor for the halogen-abstraction reaction. The fact that the electron-donating character of radicals and the electron-accepting character of tetrahalomethanes seem to be important in halogen abstraction shows that this reaction might proceed through the electron-transfer process when electron-transfer from free radicals to tetrahalomethanes is thermodynamically favorable.

Table 8. Electron Affinity/eV

CBr_4	$CBrCl_3$	CCl_4
1.2	0.68	0.15

For more quantitative information on the possibility of the electron-transfer reaction, an estimation of the difference in the redox potential between halomethanes and radicals would be helpful. The reduction potentials of CCl_4 and CBr_4 are reported to be −0.78 V and −0.30 V, respectively.26,27) Although the redox potentials of the radicals formed by a decomposition of the azo compound are not available, the oxidation potential of the hydroxymethyl radical was used which was reported to be −0.98 V.28) The redox potentials of the radicals with an electron-donating substituent, $\text{-}OC_6H_5$, $\text{-}OCOCH_3$, and $\text{-}SC_6H_5$ are considered close to that of the hydroxymethyl radical. This value suggests that the electron transfer from these radicals to tetrahalomethane, especially CBr_4, is thermodynamically possible($\Delta G = -0.6$ eV for CBr_4 and $\Delta G = -0.2$ eV for CCl_4).

Although k_x of the reaction of $(CH_3)_2\dot{C}CN$ and $(CH_3)_2\dot{C}C_6H_5$ with CBr_4 and CCl_3Br have been succesfully determined, k_x with CCl_4 was not determined, because the concentration of the adduct of $CCl_3\cdot$ was so small that the rate constants of the Cl-abstraction of these radicals could not be determined by the ESR measurement. The rate constants with CCl_4 are presumed to be less than k_x for $(CH_3)_2\dot{C}CN$ and $CBrCl_3$, being less than 10^3 M^{-1} s^{-1}. Really, k_x for the reaction of $CH_3\cdot$ with CCl_4 has been reported to be 3.3×10^2 M^{-1} s^{-1} at 65 °C.29,30) Therefore, it is concluded that the rate constant for the halogen abstraction of these radicals from CBr_4 is more than 100 times as large as that from CCl_4. The large difference in the absolute rate constants between CBr_4 and CCl_4 is probably explained by participation of electron transfer from these radicals to CBr_4 in the halogen-abstraction reaction.

Next, we investigated the difference in k_x's for each radical between CCl_4 and $CBrCl_3$. In the $(CH_3)_2\dot{C}CN$ radical, k_x for Br abstraction from CBr_4 was 24-times larger than that for $CBrCl_3$, while in the $(CH_3)_2\dot{C}C_6H_5$ radical k_x from CBr_4 was four times larger than that from $CBrCl_3$. The ionization potential of the $(CH_3)_2\dot{C}C_6H_5$ radical is considered to be smaller than that of the $(CH_3)_2\dot{C}CN$ radical, because the cyano group is more electron-accepting than the phenyl group. Therefore, these results suggest that the electron transfer from the $(CH_3)_2\dot{C}CN$ radical to $CBrCl_3$ might be thermodynamically difficult and, that in the other three cases, electron-transfer reactions are thermodynamically favorable. This presumption reasonably explains the smaller difference in k_x for $(CH_3)_2\dot{C}C_6H_5$ between CBr_4 and $CBrCl_3$ because in this radical the rate constants are considered to be mainly controlled by the difference in the dissociation energy of the C–Br bond between radical anions obtained by an electron-transfer reaction.

Reliability of Rate Constants. Let us discuss the reliability of k_1 and k_3. The k_1 values are 10—10^3 times larger than the propagation rate constants of vinyl compounds.[31] This fact is reasonably explained by the fact that 2-*t*-(butylthio)acrylonitrile is a strong radical scavenger due to its stabilizing effect of captodative substituent.[13] The k_3 values are one order of magnitude smaller than those of the self-coupling reaction of carbon radicals such as $(CH_3)_2\dot{C}CN$ and $(CH_3)_2\dot{C}C_6H_5$.[20,21] This result can be reasonably explained by the stabilization of the adduct due to the capto-dative substituent effect.[13]

There are only a little available data regarding the elementary rate constants for the halogen-abstraction of carbon radicals from tetrahalomethanes, except for CCl_4:[10,11,30] k_x of the halogen abstraction reaction of $CH_3\cdot$ from $CBrCl_3$ was reported to be $2.2\times10^6\ M^{-1}\ s^{-1}$ at 65 °C.[30] On the assumption that the activation energy for the reaction is 5—10 kcal mol^{-1},[32] k_x at 80 °C are calculated to be the range of 3.0×10^6—$4.2\times10^6\ M^{-1}\ s^{-1}$. The k_x value for $(CH_3)_2\dot{C}C_6H_5$ obtained by our experiments are one order of magnitude less than the calculated values, which can be reasonably explained by the difference in the steric factor.

Thus, the spin-trapping method is considered to be applicable to a determination of the rate constants for a halogen-abstraction reaction and the chain-transfer reaction in radical polymerizations.

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